

Part I. The Interaction of Phenylarsine with
Phenylhaloarsines. Part II. Diarsyls IV.
The Interaction of Diphenyldiiododiarsyl
with Alkali, with Phenylarsine and
with Diphenylarsine

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE
UNIVERSITY OF MICHIGAN

By
L. D. Powers
1932

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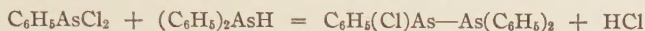
The author wishes to express his indebtedness to Prof. F. F. Blicke who suggested the subject of this thesis and who aided him constantly during the investigation by many valuable suggestions.



PART I

THE INTERACTION OF PHENYLARSINES WITH PHENYLHALOARSINES

Several years ago it was announced by Steinkopf and Smie¹ that phenyldichloroarsine and diphenylarsine react to form triphenylchlorodiarsyl.

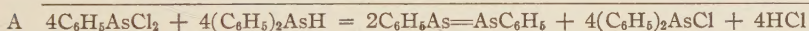
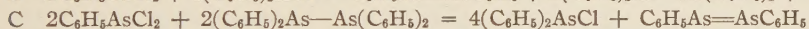
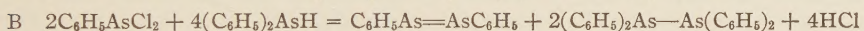


Since we wished to prepare triphenylhydroxydiarsyl,² hydrolysis of the corresponding chloro compound suggested itself as a preparative procedure. Phenyldichloroarsine and diphenylarsine were allowed to react in the proportions used by the above-mentioned investigators but instead of triphenylchlorodiarsyl, arsenobenzene and diphenylchloroarsine were obtained in yields which correspond closely to those calculated from equation A.³



The reaction between diphenylarsine, as well as phenylarsine, and each of the following compounds was then investigated: phenyldichloroarsine, phenyldi-iodoarsine, diphenylchloroarsine and diphenyliodoarsine.

It has been shown in separate experiments that two molecular equivalents of phenyldichloroarsine and four equivalents of diphenylarsine yield arsenobenzene and tetraphenyldiarsyl (B), that equivalent amounts



of phenyldichloroarsine and tetraphenyldiarsyl react to form diphenylchloroarsine and arsenobenzene (C) and that no reaction takes place at ordinary temperature between diphenylchloroarsine and arsenobenzene or between diphenylarsine and arsenobenzene.

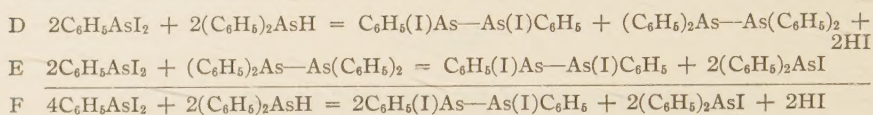
When phenyldi-iodoarsine is allowed to react with diphenylarsine in the ratio shown in formulation F diphenyldi-iododiarsyl and diphenyl-

¹ Steinkopf and Smie, *Ber.*, **59**, 1459 (1926).

² It is of interest to note that Wieland and co-workers [*Ber.*, **44**, 898 (1911); *ibid.*, **48**, 1118 (1915)] were unable to obtain the corresponding nitrogen analog $\text{R}_2\text{N}-\text{NR}(\text{OH})$.

³ The very unsharp melting point (164–179°) of the "triphenylchlorodiarsyl" obtained by Steinkopf and Smie indicates that these investigators really had a mixture of compounds. The identity of the material obtained by them was based on the result of a chlorine analysis and on the fact that phenylarsonic acid and diphenylarsonic acid were obtained upon oxidation of the reaction product. Obviously, the same data would be obtained from a mixture which consisted of arsenobenzene and twice the molecular quantity of diphenylchloroarsine.

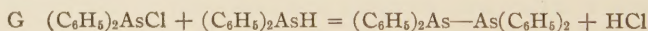
iodoarsine are formed. The di-iododiarsyl is produced in this instance



due to the fact that phenyldi-iodoarsine, unlike phenyldichloroarsine, reacts at ordinary temperature with arsenobenzene.⁴ The mechanism of this reaction may, possibly, be explained on the basis of reactions D and E since these reactions have been established by separate experiments.

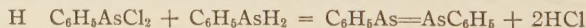
Steinkopf and Smie⁵ mixed phenyldi-iodoarsine and diphenylarsine in the ratio expressed in formulation D and stated that phenyliodoarsine, $\text{C}_6\text{H}_5\text{As}(\text{I})\text{H}$, and diphenyliodoarsine were produced. The "phenyliodoarsine" described by them was, undoubtedly, diphenyldi-iododiarsyl. Furthermore, these investigators stated⁶ that one molecular equivalent of phenyldi-iodoarsine and two equivalents of diphenylarsine react to form pentaphenyltriarsine, $(\text{C}_6\text{H}_5)_2\text{As}-\text{As}(\text{C}_6\text{H}_5)-\text{As}(\text{C}_6\text{H}_5)_2$; neither melting point nor any other property of this compound was recorded. The nature of the reaction product was merely deduced from the fact that treatment of the reaction product with iodine yielded phenyldi-iodoarsine and diphenyliodoarsine in a certain ratio. The experimental data yield little or no evidence in favor of the contention that pentaphenyltriarsine was formed in this reaction.

Diphenylchloroarsine and diphenylarsine, dissolved in ether, yielded tetraphenyldiarsyl and the interaction of these substances represents a satisfactory method for the preparation of the diarsyl.

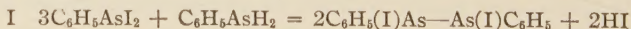


Diphenyliodoarsine and diphenylarsine, dissolved in alcohol, also react to form tetraphenyldiarsyl.

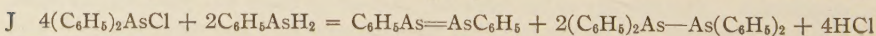
Phenyldichloroarsine reacts with phenylarsine to form arsenobenzene.



Phenyldi-iodoarsine and phenylarsine yield the same reaction product when they are mixed in equivalent amounts. However, if three molecular equivalents of the di-iodo compound react with one equivalent of phenylarsine diphenyldi-iododiarsyl is formed.



When diphenylchloroarsine and phenylarsine are allowed to react in the ratio expressed in the following equation arsenobenzene and tetra-



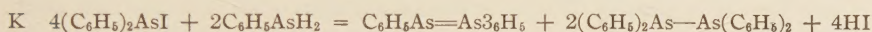
⁴ Blicke and Smith, *J. Am. Chem. Soc.*, **52**, 2942 (1930).

⁵ Ref. 2, p. 1460.

⁶ Ref. 2, p. 1461.

phenyldiarsyl are produced. If the above-mentioned compounds are mixed in equimolecular quantities arsenobenzene and tetraphenyldiarsyl are again formed as reaction products. Steinkopf and Smie⁷ stated that diphenylchloroarsine and phenylarsine react to form triphenyldiarsyl, $(C_6H_5)_2As-As(H)C_6H_5$. These investigators merely analyzed their reaction product, which was not characterized by a melting point, and considered the arsenic analysis and the fact that a mixture of phenylarsonic and diphenylarsinic acids was obtained upon oxidation of their product with nitric acid sufficient proof for the claim that triphenyldiarsyl had been formed. The data published by Steinkopf and Smie would be almost identical with that obtained from a mixture which consisted of one equivalent of arsenobenzene and two equivalents of tetraphenyldiarsyl.

Diphenyliodoarsine and phenylarsine, mixed in the proportion given below, yield arsenobenzene and tetraphenyldiarsyl.



Experimental Part

Since phenylarsine, diphenylarsine and many of the reaction products absorb oxygen with great rapidity, it was necessary to carry out all experiments in an inert atmosphere. The apparatus used for this purpose is shown in the accompanying sketch. By manipulation of the stopcocks the free radical bulb, as well as the buret above it, was evacuated and filled with dry, oxygen-free nitrogen. This operation was repeated several times until all air had been removed from the system. The arsine was introduced into the buret from the reservoir⁸ and allowed to flow into the evacuated radical bulb. The walls of the buret were then washed free from arsine by the introduction of ether, benzene or alcohol from the dropping funnel. After the radical bulb had been filled with nitrogen, it was disconnected and the substance added with which the arsine was to react.⁹ In the event that pressure developed in the bulb the side arm of the latter was connected to the mercury trap shown in the lower left-hand corner of the diagram.

All solvents were saturated with nitrogen prior to use and only the absolute grades of alcohol and ether were employed. A dextrin-mannitol-glycerol stopcock lubricant¹⁰ was found to be very satisfactory when ether or benzene was used as a solvent. The melting points of compounds which absorb oxygen were determined in a sealed tube filled with nitrogen. The reaction mixtures were shaken for at least twenty-four hours. Absorption experiments were carried out in bromobenzene solution.

Phenyldichloroarsine and Diphenylarsine (A, B).—Six and ninety-two hundredths

⁷ Ref. 2, p. 1458.

⁸ After each arsine had been prepared it was distilled directly into a reservoir of the type shown through the short side arm. In such containers the arsines can be protected from oxidation for a long time.

⁹ In some instances the arsine was introduced after the other component of the reaction had been placed in the radical bulb.

¹⁰ C. C. Meloche and W. G. Fredrick, *J. Am. Chem. Soc.*, **54**, 3264(1932).

grams (5.32 cc., 0.030 mole) of diphenylarsine¹¹ was added to 8.50 g. (0.038 mole) of phenyldichloroarsine, dissolved in 50 cc. of ether. After a short time a heavy, crystalline precipitate had formed. The ether was decanted into a second radical bulb and the precipitate, which proved to be arsenobenzene, washed with ether a number of times until it was entirely free from halogen compounds;¹² mixed m. p. 210–212°. The material was recrystallized from xylene for analysis.

Anal. Calcd. for $C_{12}H_{10}As_2$: As, 49.31.
Found: As, 49.23, 49.38.

The yield was 3.96 g. or 87% of the calcd. amount.

The ether layer from the reaction mixture, which contained diphenylchloroarsine and unchanged phenyldichloroarsine, was treated with alkali in order to convert the chlorides into oxides. Phenylarsine oxide dissolved in the aqueous layer while 6.78 g. or 95% of the calcd. amount of tetraphenylarsyl oxide was isolated from the ether layer. The latter oxide, after it had been washed with petroleum ether (30–60°), melted at 94–95°.

Mixed in the ratio shown in formulation B, 4.6 g. (3.5 cc., 0.02 mole) of diphenylarsine reacted with 2.2 g. (0.01 mole) of phenyldichloroarsine, dissolved in 25 cc. of ether, to form a bulky, crystalline precipitate. In order to expel the hydrogen chloride formed¹³ the ether was removed by distillation, the residue treated with 25 cc. of ether and the solvent again expelled. After the product had been dried for two hours under 15 mm. pressure the mixture was extracted a number of times with ether in order to remove tetraphenyldiarsyl; about 500 cc. of ether was used for this purpose. The tetra-phenyldiarsyl obtained melted at 125–129°;¹⁴ 0.887 g. of the material absorbed 43 cc. (N. T. P.) of oxygen, which is the calculated amount. The arsenobenzene, which remained as a residue, weighed 1.3 g.; calcd. amount 1.5 g.; mixed m. p. 209–211°.

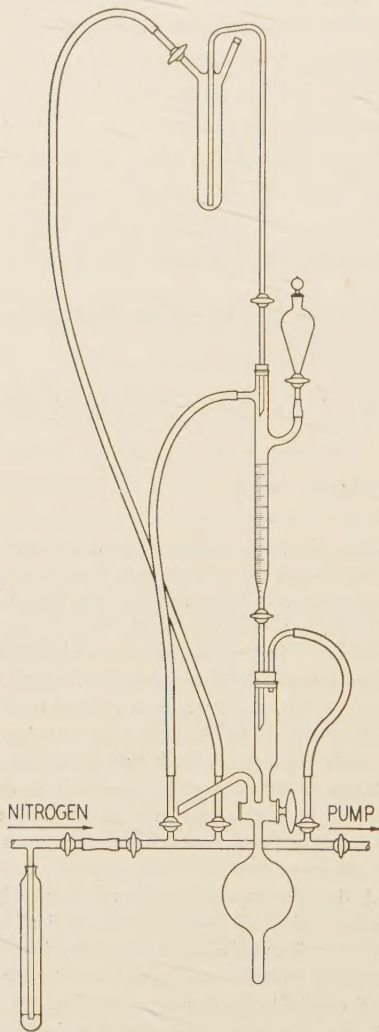


Fig. 1.

¹¹ The following constants were determined for diphenylarsine: d_{25}^{25} 1.30; b. p. 158–160° under 16 mm. pressure.

¹² Arsenobenzene absorbs oxygen rapidly unless it is washed free from all traces of halogen compounds.

¹³ Removal of the hydrogen chloride seems to facilitate the quantitative isolation of arsenobenzene and also prevents oxidation of the latter.

¹⁴ Blicke and Smith, *J. Am. Chem. Soc.*, **51**, 2275 (1929); Blicke, Weinkauff and Hargreaves, *ibid.*, **52**, 782 (1930).

Phenyldichloroarsine and Tetraphenyldiarsyl (C).—Two and forty-five hundredths grams (0.005 mole) of tetraphenyldiarsyl was allowed to react with 1.2 g. (0.005 mole) of phenyldichloroarsine, dissolved in 100 cc. of ether. About three-fourths of the solvent was then removed by distillation and after some time a precipitate of arsenobenzene was obtained. The supernatant liquid was decanted and the arsenobenzene washed free from chlorine compounds with ether. There was isolated 0.22 g. of the arseno compound which melted at 196–206°. The ether washings were exposed to air and the residue obtained after evaporation of the solvent was treated with a mixture of ether and low-boiling petroleum ether; 0.92 g. of diphenylchloroarsine, m. p. 41–42°, was obtained.

Phenyldi-iodoarsine and Diphenylarsine (D, F).—Diphenyldi-iododiarsyl precipitated almost immediately when 4.06 g. (0.01 mole) of phenyldi-iodoarsine, dissolved in 100 cc. of ether, was mixed with 2.30 g. (0.01 mole) of diphenylarsine. After twenty-four hours the solvent was completely removed by distillation and the residue, a mixture of diphenyldi-iododiarsyl and tetraphenyldiarsyl, dried for two hours under diminished pressure in order to expel hydrogen iodide. The mixture was extracted four times with 50-cc. portions of ether and the ether layers, which contained tetraphenyldiarsyl, decanted into a second radical bulb. The residue of diphenyldi-iododiarsyl weighed 2.43 g.; calcd. amount 2.79 g.; m. p. 176–179°. ¹⁵

The combined ether extracts were shaken with alkali to remove traces of iodine compounds and the solvent then removed. An oil was obtained which was treated with 25 cc. of alcohol; after the solvent had been partially removed by distillation tetraphenyldiarsyl separated in crystalline form. After recrystallization from absolute alcohol, 1.3 g. of material was obtained which melted at 128–130°.

Anal. Calcd. for $C_{24}H_{20}As_2$: As, 32.73. Found: As, 32.58, 32.28.

From the alcoholic mother liquor 0.4 g. more of the diarsyl was obtained. The calcd. yield is 2.29 g. Upon exposure to oxygen, 0.587 g. of the compound absorbed 30 cc. (N. T. P.) of the gas; calcd. amount 29 cc.

In accordance with formulation F 2.30 g. (0.01 mole) of diphenylarsine was added to 8.11 g. (0.02 mole) of phenyldi-iodoarsine, dissolved in 50 cc. of ether. A copious yellow precipitate of diphenyldi-iododiarsyl formed immediately. The ether layer was decanted, the precipitate washed a number of times with ether and then dried at 50° under 15 mm. pressure for two hours. The product melted at 177–178°; yield 5.32 g.; calcd. yield 5.57 g. From the ether mother liquor an oil was obtained which solidified in the form of a yellow crystalline mass when cooled; m. p. 39–41°. This material, diphenyliodoarsine, weighed 3.76 g. in the crude state; calcd. yield 3.55 g.

Phenyldi-iodoarsine and Tetraphenyldiarsyl (E).—Four and one-tenth grams of phenyldi-iodoarsine was added to about 2 g. of tetraphenyldiarsyl, dissolved in benzene. Diphenyldi-iododiarsyl soon precipitated from the mixture; after it had been washed with ether it melted at 175–177° and weighed 1.4 g. The benzene mother liquor and ether washings were combined and shaken with alkali in order to convert the halides to oxides. The diphenyliodoarsine was isolated, therefore, as tetraphenylarsyl oxide; yield 1.4 g. Eight-tenths of a gram of phenylarsine oxide was also obtained as the result of hydrolysis of the excess phenyldi-iodoarsine used.

Diphenylchloroarsine and Diphenylarsine (G).—To 3.4 g. (0.015 mole) of diphenylarsine there was added 4.4 g. (0.016 mole) of diphenylchloroarsine, dissolved in 50 cc. of ether. After two hours the solution was concentrated to a volume of about 10 cc., whereupon tetraphenyldiarsyl precipitated. The ether mother liquor was decanted, a small quantity of fresh ether added and the ether suspension shaken a number of times

¹⁵ Blicke and Smith, *J. Am. Chem. Soc.*, **52**, 2943 (1930).

with water until all hydrochloric acid had been removed. The ether was then removed by distillation and the material dried under diminished pressure; m. p. 124–127°. The yield was 6.0 g.; calcd. yield, 6.8 g.

Diphenyliodoarsine and Diphenylarsine.—Tetraphenyldiarsyl precipitated instantly when 3.56 g. of diphenyliodoarsine, dissolved in 50 cc. of alcohol, was added to 2.30 g. of diphenylarsine. The diarsyl was purified in the manner described above; m. p. 129–130°. The yield was 3.4 g.; calcd. amount, 4.6 g.

Phenyldichloroarsine and Phenylarsine (H).—A mixture prepared from 3.34 g. (0.015 mole) of phenyldichloroarsine, 2.30 g. (0.015 mole) of phenylarsine and 65 cc. of ether was shaken for twenty-four hours. The ether layer was decanted from the crystalline material into a second radical bulb and the solid product washed with ether until it was completely free from hydrogen chloride. The material, which was arsenobenzene, weighed 1.94 g.; m. p. 209–211°. From the ether layer 2.20 g. more of arsenobenzene was obtained. The total yield was 4.14 g.; calcd. amount, 4.56 g.

Phenyldi-iodoarsine and Phenylarsine (I).—No apparent reaction took place after 2.30 g. (0.015 mole) of phenylarsine had been shaken with 1.68 g. (0.01 mole) of phenylarsine oxide, dissolved in benzene, for twenty-four hours.¹⁶ There was then added 12.2 g. (0.03 mole) of phenyldi-iodoarsine, dissolved in benzene. Diphenyldi-iododiarsyl precipitated immediately; m. p. 178–180°. The yield was 14.3 g.; calcd. yield, based on 0.04 mole of phenyldi-iodoarsine, 14.8 g.

Diphenylchloroarsine and Phenylarsine (J).—When 12 g. (0.045 mole) of diphenylchloroarsine was added to 2.97 g. (0.019 mole) of phenylarsine, dissolved in 100 cc. of ether, there was no visible sign of reaction. Twenty-five cubic centimeters of alcohol was then added, whereupon a crystalline precipitate soon began to form. After twelve hours the solvents were removed by distillation and the residue dried for two hours under 15 mm. pressure in order to remove hydrogen chloride completely. One hundred cubic centimeters of ether was added to the residue, the mixture shaken for several hours and the ether solution of tetraphenyldiarsyl decanted into a second radical bulb. This process was repeated until a test portion of the ether extract left no residue upon evaporation of the solvent; about 500 cc. of ether was required. From the ether solutions there was obtained 9.08 g. of tetraphenyldiarsyl; m. p. 123–127°; calcd. yield 9.16 g. When 0.915 g. of the compound was exposed to oxygen, 47 cc. of the gas was absorbed; calcd. absorption, 45 cc. The residue after extraction of the reaction mixture with ether was pure arsenobenzene; m. p. 210–211°. The yield was 2.70 g.; calcd. yield, 3.04 g.

Anal. Calcd. for $C_{12}H_{10}As_2$: As, 49.31. Found: As, 49.57, 49.23.

In the following experiment the compounds were allowed to react in amounts which are practically equimolecular. To 5.29 g. (0.020 mole) of diphenylchloroarsine, dissolved in 100 cc. of alcohol, there was added 3.24 g. (0.021 mole) of phenylarsine; an oil precipitated which soon became crystalline. The alcohol layer was decanted into a second bulb and after complete removal of hydrogen chloride and unchanged arsine the tetraphenyldiarsyl was extracted with ether; m. p. 123–130°. The yield was 2.33 g.; calcd. yield, 4.58 g. One and fifty-four hundredths grams of arsenobenzene, m. p. 207–210°, was left as a residue; calcd. amount, 1.52 g.

The alcoholic solution which had been decanted contained the remainder of the diarsyl; the latter was allowed to oxidize in air. The alcohol was removed, the mixture of diphenylarsinic acid and tetraphenylarsyl oxide treated with sulfur dioxide and

¹⁶ These compounds were mixed in order to determine whether or not they reacted under the given experimental conditions. The hydrogen iodide, formed subsequently as a result of the interaction of phenylarsine and phenyldi-iodoarsine, converted the phenylarsine oxide into phenyldi-iodoarsine.

hydriodic acid in the presence of hydrochloric acid and the diphenylhaloarsines hydrolyzed to tetraphenylarsyl oxide; yield, 1.93 g.; m. p. 92–95°.

Any pentaphenyltriarsine or triphenyldiarsyl which might have been formed in this reaction would have been present in the decanted alcoholic solution and upon oxidation would have been converted into tetraphenylarsyl oxide and phenylarsine oxide; only a trace of the latter was found to be present in the oxidized solution.

Diphenyliodoarsine and Phenylarsine (K).—No apparent reaction took place when 8.50 g. (0.024 mole)¹⁷ of diphenyliodoarsine was mixed with 1.08 g. (0.007 mole) of phenylarsine in 100 cc. of ether. Upon the addition of 25 cc. of alcohol a precipitate soon formed. After forty-eight hours the supernatant liquid was decanted into a second bulb and the precipitated arsenobenzene washed six times with 50-cc. portions of ether; m. p. 200–204°. The yield was 0.93 g.; calcd. yield, 1.07 g.

The ether–alcohol layer which had been decanted contained tetraphenyldiarsyl and the excess diphenyliodoarsine. The solution was concentrated to about 15 cc., whereupon tetraphenyldiarsyl and some diphenyliodoarsine precipitated. The mother liquor was decanted and the product washed a number of times with petroleum ether (30–60°) in order to remove the iodoarsine. The yield of tetraphenyldiarsyl was 1.40 g.; m. p. 129–130°; calcd. amount, 3.21 g.

Each of the following compounds, dissolved in ether, was shaken with arsenobenzene for three days at ordinary temperature: phenyldichloroarsine, diphenylchloroarsine, diphenyliodoarsine, diphenylarsine and phenylarsine. In the case of each mixture at least 90% of each component was recovered unchanged. Furthermore, it was found that neither phenylarsine nor diphenylarsine reacts with tetraphenyldiarsyl at ordinary temperature.

Summary

The interaction of phenylarsine, as well as diphenylarsine, and each of the following compounds has been investigated: phenyldichloroarsine, phenyldi-iodoarsine, diphenylchloroarsine and diphenyliodoarsine. Substances such as tetraphenyldiarsyl, diphenyldi-iododiarsyl and arsenobenzene have been obtained as reaction products.

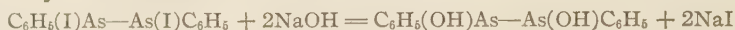
It seems that compounds such as phenyliodoarsine, triphenyldiarsyl, triphenylchlorodiarsyl and pentaphenyltriarsine are not produced by interaction of the above-mentioned arsines although the formation of these substances has been reported by other investigators.

¹⁷ This quantity represents an excess over that demanded by the formulation

PART II

DIARSYLS. IV. THE INTERACTION OF DIPHENYLDIIODODIARSYL WITH ALKALI, WITH PHENYLARSINE AND WITH DIPHENYLARSINE

It seemed that diphenyldihydroxydiarsyl, a substance which has never been described, should be produced from the interaction of diphenyldiododiarsyl¹ and alkali



Diphenyldiododiarsyl, suspended in ether, was shaken with excess sodium hydroxide solution in a free radical apparatus filled with nitrogen. The halogen was removed rapidly and quantitatively from the diarsyl and a crystalline, alkali-insoluble material remained partly dissolved and partly suspended in the ether layer. Upon separation and acidification of the alkaline solution a considerable amount of phenylarsine oxide was obtained. The alkali-insoluble product, after it had been recrystallized twice from benzene, possessed properties which in some respects resembled those of arsenobenzene; in certain other characteristics, however, the material was decidedly dissimilar to this substance as is shown by the following tabulation.

ALKALI-INSOLUBLE PRODUCT	ARSENOBENZENE
Separates from a benzene solution in the form of large, granular crystals	Separates from a benzene solution in the form of fine needles
M. p. 195–197°. ^a Mixed with arsenobenzene, m. p. 190–195° ^b	M. p. 210–212°
Mol. wt., 603°	Mol. wt. 867; ^d calcd. 304
% As, 47.12°	% As, 49.31
Absorbs oxygen rapidly ^f	Does not absorb oxygen
Dissolves rapidly in ether upon the addition of HCl or HBr; arsenobenzene precipitates quickly from the solution	Does not dissolve in ether upon the addition of a halogen acid
One hundred cubic centimeters of boiling benzene dissolve 7.9 g. of the material	One hundred cubic centimeters of boiling benzene dissolve 1.4 g. of this compound
Yields diphenyldiododiarsyl when treated with iodine in ether	Yields diphenyldiododiarsyl when treated with iodine in ether

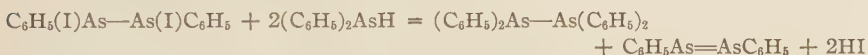
^{a, b} The melting point was determined in a sealed tube filled with nitrogen. ^c This result represents the average of six determinations on three different samples of material. The determinations were made in boiling benzene in a stream of nitrogen. ^d This value was obtained in boiling benzene in a stream of nitrogen; previously the molecular weight had been found to be 895 and 915, under the same experimental conditions [Blicke and Smith, *J. Am. Chem. Soc.*, **52**, 2950 (1930)]. ^e This figure represents the average value of six analyses made with three different samples of material. ^f 1.042 g. of the product absorbed 73 cc. (N. T. P.) of oxygen in five minutes.

(1) Blicke and Smith, *J. Am. Chem. Soc.* **52**, 2937 (1930).

Diphenyldibromodiarsyl, when hydrolyzed, yielded products identical with those obtained from diphenyldiiododiarsyl. Di-*p*-anisylidiiododiarsyl yielded *p*-anisylarsine oxide and an alkali-insoluble compound which, to some extent, resembled di-*p*-methoxyarsenobenzene, yet seemed to be different from this material.

It has been claimed by Steinkopf and Smie² that diphenyldiiododiarsyl, suspended in alcohol, reacts with diphenylarsine at 70° to form hexaphenyltetraarsine (C₆H₅)₂As—As(C₆H₅)—As(C₆H₅)—As(C₆H₅)₂. The only experimental fact offered in support of this structure was an arsenic analysis, which differed from the calculated amount of arsenic by 2.98%, and the behavior of the material with iodine; in the latter reaction phenyldiiodoarsine and diphenyliodoarsine were formed in approximately equivalent amounts. No melting point was recorded and the above mentioned investigators admitted that their product was impure.

We have found that the compounds under discussion react at ordinary temperature in an entirely different manner, namely, with the formation of tetraphenyldiarsyl and arsenobenzene. Such a mixture would, of course, contain the same amount of arsenic as hexaphenyltetraarsine and, upon treatment with iodine, would yield phenyldiiodoarsine and diphenyliodoarsine in equivalent amounts. It seems very probable that the tetraarsine of Steinkopf and Smie was, in reality, a mixture of tetraphenyldiarsyl and arsenobenzene.



Diphenyldiiododiarsyl and phenylarsine react to form arsenobenzene



Steinkopf and Smie² stated that these compounds yield cyclic triphenyltriarsine, $\text{C}_6\text{H}_5\text{As—}\underbrace{\text{As}(\text{C}_6\text{H}_5)\text{—AsC}_6\text{H}_5}_{\text{—AsC}_6\text{H}_5}$, but since no melting point was reported

for the triarsine and the calculated analytical data for this compound are the same as for arsenobenzene, the alleged formation of the triarsine in this reaction seems to have been based on an insufficient amount of experimental evidence.

Experimental Part

Hydrolysis of Diphenyldi-iododiarsyl.—The diiododiarsyl was prepared from 24.4 g. of phenyldiiodoarsine,³ 50 cc. of absolute alcohol and 40 g. of crystalline phosphorous acid, dissolved in 200 cc. of alcohol. The diarsyl was then suspended in 100 cc. of ether, shaken for one hour with 100 cc. of 10% sodium hydroxide solution, the alkaline layer decanted and the ether layer extracted three times with 50-cc. portions of alkali. Upon neutralization of the alkaline extracts with sulfuric acid in a nitrogen atmosphere,

(2) Steinkopf and Smie, *Ber.*, **59**, 1462 (1926).

(3) This material, after it has been preserved for some time in a glass-stoppered bottle, becomes very dark in color and often contains a considerable amount of a crystalline product. The iodide, however, seems to undergo little, if any, decomposition if it is kept under a layer of concd. hydriodic acid.

3.8 g. of phenylarsine oxide was obtained, mixed m. p. 145–147°,⁴ after recrystallization from benzene–ether.

The ether layer, which contained suspended material, was concentrated to a volume of 15 cc. and the liquid decanted. The latter possessed a very strong odor similar to that of phenylarsine. The slightly yellow crystalline material was washed with alcohol, then with ether and dried under diminished pressure. After a second recrystallization from benzene the product, which was halogen free, weighed 3.2 g.

When 2.06 g. of the material, suspended in 50 cc. of ether, was shaken with 25 cc. of hydrobromic acid 1.13 g. of arsenobenzene, m. p. 210–212°, was obtained.

Anal. Calcd. for $C_{12}H_{10}As_2$: As, 49.31. Found: As, 49.26.

From 1.72 g. of the product, 50 cc. of ether and 1.4 g. of iodine there was produced 1.45 g. of diphenyldiiododiarisyl; m. p. 177–178°.

Hydrolysis of Di-*p*-anisylidiiododiarisyl.—When the diiododiarisyl,⁵ obtained from 13.1 g. of *p*-anisylidioarsine,⁶ was hydrolyzed in the manner described above, there was obtained 2.5 g. of *p*-anisylarsine oxide, m. p. 136–138°, and 1.7 g. of a crystalline halogen-free, alkali-insoluble product, m. p. 220–230°: % As found, 40.02 and 40.20.

Dissolved in bromobenzene 1.082 g. of the alkali-insoluble product absorbed 61 cc. of oxygen in two minutes.

When the alkali-insoluble material was suspended in ether and treated with hydrochloric or hydrobromic acid di-*p*-methoxyarsenobenzene was obtained; mixed m. p. 233–235°.⁷

Phenylarsine and Diphenyldi-iododiarisyl.⁸—To 6.79 g. (0.012) mole of diphenyldiiododiarisyl, suspended in 75 cc. of absolute alcohol, there was added 2.4 g. (1.8 cc., 0.015 mole) of phenylarsine. After the mixture had been shaken for twelve hours the deep yellow color of the diiododiarisyl had disappeared and a pale yellow compound remained suspended in the solvent. The alcohol was decanted, the solid material washed with alcohol and ether and then dried for some time in the radical bulb under diminished pressure. This material melted from 140–212° and absorbed oxygen: 0.600 g. absorbed 11 cc. in two minutes. The smallest possible amount of boiling xylene necessary to dissolve the product was introduced into the radical bulb; after two days 2.8 g. of pure arsenobenzene had separated from the solution; mixed m. p. 209–210°; calcd. yield 5.5 g.⁹

Anal. Calcd. for $C_{12}H_{10}O_2$: As, 49.31. Found: As, 49.07.

When alcohol was replaced by absolute ether in the above experiment and the mixture shaken for three days, 87% of the diiododiarisyl was recovered unchanged.

Diphenylarsine and Diphenyldiiododiarisyl.—The diphenyldiiododiarisyl, obtained from 8.12 g. (0.02 mole) of phenyldiiodoarsine, 14 g. of crystalline phosphorous acid and 100 cc. of absolute alcohol—approximately 0.01 mole¹⁰—was suspended in 60

(4) For further identification the oxide was converted into phenyldichloroarsine and the latter identified as phenylarsylene N-pentamethylenedithiocarbamate [Blicke and Oakdale, *J. Am. Chem. Soc.*, **54**, 2995 (1932). The melting point of this compound should be 183–184° instead of 173–174° as recorded previously.

(5) Blicke and Smith, *ibid.*, **52**, 2943 (1930).

(6) Blicke, Powers and Webster, *ibid.*, **54**, 2946 (1932).

(7) A sample of di-*p*-methoxyarsenobenzene, obtained by reduction of *p*-anisylarsine oxide in acetic acid with hypophosphorous acid, melted at 228–230° after recrystallization from bromobenzene.

(8) A description of the apparatus used in this and the following experiment was published previously [Blicke and Powers, *ibid.*, **54**, 3356 (1932)].

(9) The yield was, undoubtedly, lowered to a decided extent by recrystallization. In the recrystallization of pure arsenobenzene from xylene the yield of crystalline product which separated from the xylene was about 50%; only gummy material could be obtained from the mother liquor.

(10) The diiododiarisyl was not removed from the free radical bulb in which it had been prepared. In a number of instances in which the diarsyl, prepared by this method, had been isolated the yield of pure product was never less than 90% of the calcd. amount.

cc. of absolute alcohol and 4.60 g. (3.54 cc., 0.02 mole) of diphenylarsine added.¹¹ The mixture, initially yellow in color, was shaken vigorously for twelve hours; after thirty minutes it had become colorless. The alcohol was decanted from the solid material into a second radical bulb and the alcohol removed by distillation under reduced pressure. In order to separate the compounds formed, arsenobenzene and tetraphenyldiarsyl, advantage was taken of the fact that the latter substance is soluble in ether while arsenobenzene is practically insoluble in this solvent. One hundred cubic centimeters of ether was poured onto the mixture, whereupon most of the tetraphenyldiarsyl dissolved. The ether solution was then decanted through a Jena filter into the second bulb. The purpose of the filter was to retain finely divided arsenobenzene which remained suspended in the ether. The arsenobenzene was washed with ether until free from the diarsyl. The residue of arsenobenzene weighed 2.97 g.; m. p. 203–207°; calcd. yield 3.04. After recrystallization from bromobenzene it melted at 208–210°.

The ether solution in the second bulb was shaken with alkali to remove traces of unchanged iodides, washed free from alkali and then concentrated to a volume of 25 cc.; a copious precipitate of tetraphenyldiarsyl was obtained. After recrystallization from absolute alcohol, the material weighed 2.6 g., m. p. 128–130°.¹² Upon concentration of the mother liquor an additional 0.4 g. of product was obtained; calcd. yield 4.58 g.

Anal. Calcd. for $C_{24}H_{20}As_2$: As, 32.73. Found: As, 32.72, 32.69.

Summary

Several diaryldihalodiarsyls were treated with alkali whereupon an arylarsine oxide and an alkali-insoluble product were formed.

Phenylarsine and diphenyldiiododiarsyl react to form arsenobenzene; diphenylarsine and the diiododiarsyl yield arsenobenzene and tetraphenyldiarsyl. It has been claimed in the literature, on the basis of meager experimental data, that cyclic triphenyltriarsine is formed in the first instance and hexaphenyltetraarsine in the second.

(11) No reaction seemed to take place when ether was used as a solvent.

(12) Blicke, Weinkauff and Hargreaves, *J. Am. Chem. Soc.*, **52**, 782 (1930).

